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ABSTRACT

Ruthenium oxide coatings have been deposited on titanium substrates using a flood coating process. These films were heat treated for varying times and temperatures. The resulting films subsequently were characterized by performing resistivity and SEM analyses. Resistivity of the ruthenium oxide coating was found to be extremely dependent upon the firing temperature. Effect of the process conditions and formulations of the coatings on the morphology with respect to their electrical characteristics is presented. Capacitors were fabricated using plates coated with ruthenium oxide coatings. Capacitance versus heat treatment temperatures are discussed and at one firing temperature (480°C), the capacitance was 50 times the control capacitor value.

INTRODUCTION

TRANSITION METAL OXIDES

Among the oxides of the transition metals, only TiO (Morin, 1956), RuO_2 and IrO_2 (Ryden et al., 1968) are known to be metallic conductors at ambient temperature. The metal-metal distance and the radius of the cation in these oxides are such that overlap of the inner d orbitals between ruthenium and oxygen is possible, and the d electrons in the d bands are responsible for the metallic conduction (Morin, 1956; Marcus, 1968; Rogers, *et al.*, 1969; Trasatti and Buzzanca, 1971; Boman, 1970; Baur, 1956; Avdeev, *et al.*, 1971; Ryden, *et al.*, 1970; Schaefer, *et al.*, 1963; Erenburg, *et al.*, 1972; Chu, 1970; and Galizzioli, 1975).

Ruthenium oxide, in comparison with other metallic oxides, presents the advantage of preparation at relatively low temperatures. It can be deposited easily as a film a few micrometers thick on an inert metallic support. The low temperature of preparation makes the oxidation of the support and possible interdiffusion at the solid interface negligible.

The d-electron configuration for the cations, if the oxides are considered to be fully ionic, is $4d^4$ for ruthenium (Ryden *et al.*, 1968). The resistivity, at room temperature, of intrinsic RuO_2 is 3.5×10^{-5} ohm x cm (Ryden and Lawson, 1970). This resistivity value will cause little ohmic resistance in a film of one to two micrometers thick, but the value does suggest that the films are semiconductors which are reasonably assumed to be n-type (Kuhn and Mortimer, 1973).

In the rutile structure, the metal atoms are placed at the cell center and the body center of the crystal (Fig. 1). The metal atoms are coordinated very nearly octahedrally by oxygen, with one axis of the octahedron being 2% shorter than the others. Four of the six Ru-O distances are 1.984 ± .006 Å and the other two are 1.942 ± .010 Å. The shortest Ru-Ru distance is 3.107 Å which precludes any significant metal-metal interaction.

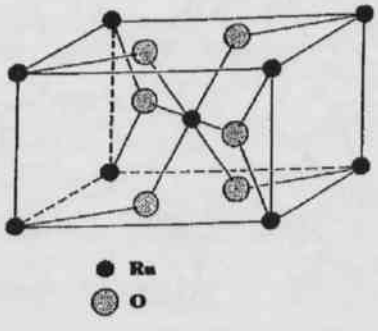

Figure 1. Unit cell in intrinsic rutile. Small black balls are ruthenium atoms and the chocked larger balls are oxygen atoms

Rare-earth oxide coated titanium substrates are widely used in the chlor-alkali industry for the production of chlorine in saturated acidified brine at 70°C (Arikado *et al.*, 1977; O'Grady *et al.*, 1974; De Nora, 1970; De Nora, 1971; Beer, 1968; and Kuhn and Mortimer, 1972). This electrochemical process is one of the harshest environments to which an electrode can be subjected. The ruthenium oxide layer on the surface of a titanium electrode inhibits passivation of the titanium and acts as an excellent electronic conductor at the electrode side of the electrode-solution interface. Additionally, rare-earth composites, and in particular RuO_2, show exceptional mechanical stability.

Numerous oxide coatings for titanium have been developed. The vast majority are based on RuO_2 with the addition of various other rutile oxides. The basic coating is formed from a solution of $RuCl_3$, HCl, butanol, and n-butyl titanate $Ti(OBu)_4$ in various proportions. Acid-cleaned (HCl, 6.0M, one minute) titanium substrates are dipped into this solution and oven-fried at 400-500°C for 5 to 30 minutes depending on the specific coating desired. During the pyrolyzing of the coating mixture, the surface of the titanium also is pyrolyzed to a mixed $TiO\text{-}TiO_2$. This compound is essentially rutile in nature and forms a diffuse interface with the coating material.

EXPERIMENTAL

RUTHENIUM OXIDE COATING PROCEDURES

Titanium squares (one inch x one inch x .035 inch) were completely liquid coated on one side only (flood coated) with solutions of $RuCl_3$, HCl, butanol, and n-butyl titanate $Ti(OBu)_4$ in various proportions. After liquid coating of the titanium squares, the squares were air dried for twenty-four hours. The air dried squares then were fired in the temperature range of 475 - 495°C for time periods ranging from 5 - 20 minutes in a Lindberg Type 51333 oven equipped with a Lindberg Eurotherm Controller/Programmer Type 813. Firing temperature was found to be very critical in guaranteeing an integral and mechanically stable coating on the titanium squares. The optimum firing time was found to be eight minutes. The final optimum coating formulation mixture was: 3.0 gms of ruthenium metal as $RuCl_3 \times 3H_2O$, 3.0 ml of concentrated HCl, 46.0 ml of butanol, and 22.0 gms of n-butyl titanate. Additional coats were applied by repeating the coating, air drying, and firing procedure. Three coats were applied to all titanium squares that were measured for resistance and capacitance.

All four probe resistivity measurements used a Keithley Model 224

Programmable Current Source, a Keithley Model 617 Programmable Electrometer, and a four probe head from Alessi. The four probe head was a spring loaded constant pressure head mounted in a Cambridge Thermionic Corporation pressure swager yoke. After final coating and firing, two titanium squares were placed in a home-built Plexiglas fixture. Polyethylene film (2 mil) was used as the dielectric whereupon the two plates were forced together with four screws in the fixture. Access holes were drilled in the fixture to allow connection for capacitance measurements. Capacitance measurements used a General Radio Model 1200 Capacitance Bridge operated at 1.0 kHz. All SEMs were made using a Cambridge Instruments Steroscan 600.

RESULTS AND DISCUSSION

The firing temperature has a profound affect upon the ruthenium oxide morphology as shown by the SEM's in Figs. 3-6. The final appearance was dark violet or purple to black with a slight metallic luster. As can be seen, the coatings have the appearance of a mud-cracked, dried out lake bottom. The unique properties of the ruthenium oxide coatings can be attributed to both its low electrical resistivity, as well as the apparent increased surface area. No stoichiometric analyses were performed to determine the exact Ru/O ratios for the coats that were formed. The morphology (in going from 475°C to 490°C) clearly demonstrates that the individual oxide plates were diminishing in average size, that is, the surface became more cracked. However, whether the cracking depth varied concomitantly was not ascertained. The changes in morphology with increasing temperature followed the dramatic drop in resistivity as shown in Fig. 7. The control line is the resistivity value measured on a cleaned titanium square and shown in Fig. 2. All data points are the average of six resistivity values that were measured at random locations on the coated squares. Since no determinations were made of composition or purity, the

Figure 2. SEMof a cleaned titanium square at 200 x.

resistivity changes may not be reflective of heating effects, but may indicate sample impurities (for example, Cl^-) or structural defects. Additional resistivity measurements are in progress as a function of not only firing temperature, but firing time to determine the optimum parameter to minimize coating resistivity.

Figure 3. Three coated surface fired at 475°C for eight minutes at 200 x

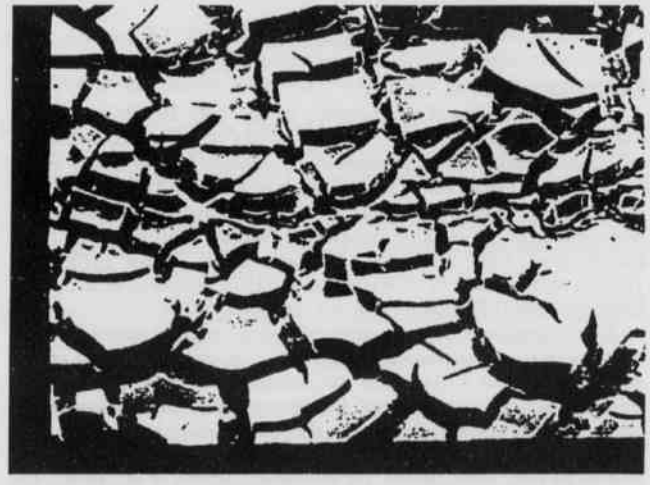

Figure 4. Three coated surface fired at 480°C for eight minutes at 200 x.

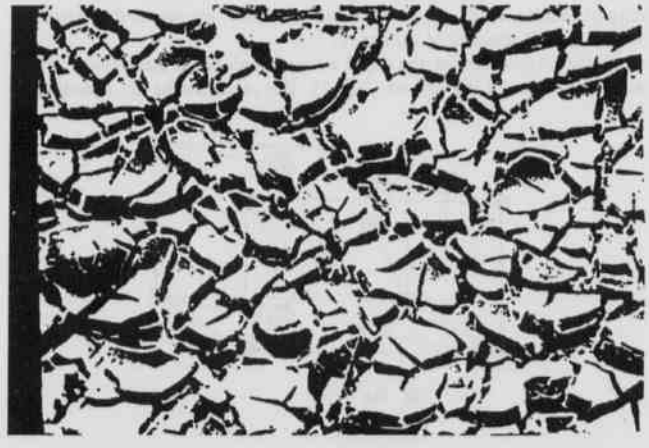

Figure 5. Three coated surface fired at 485°C for eight minutes at 200 x.

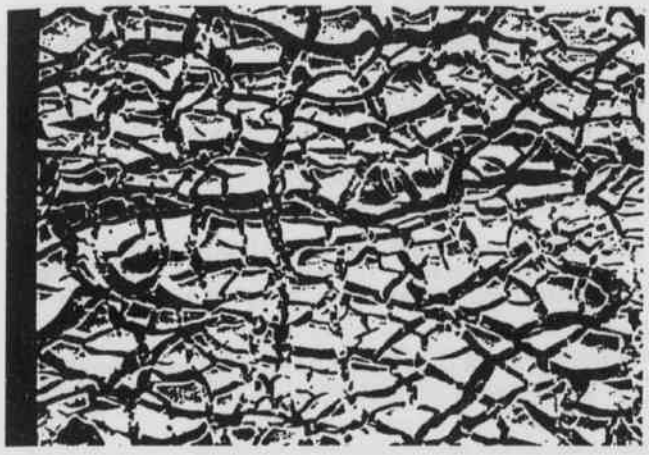

Figure 6. Three coated surface fired at 490°C for eight minutes at 200 x.

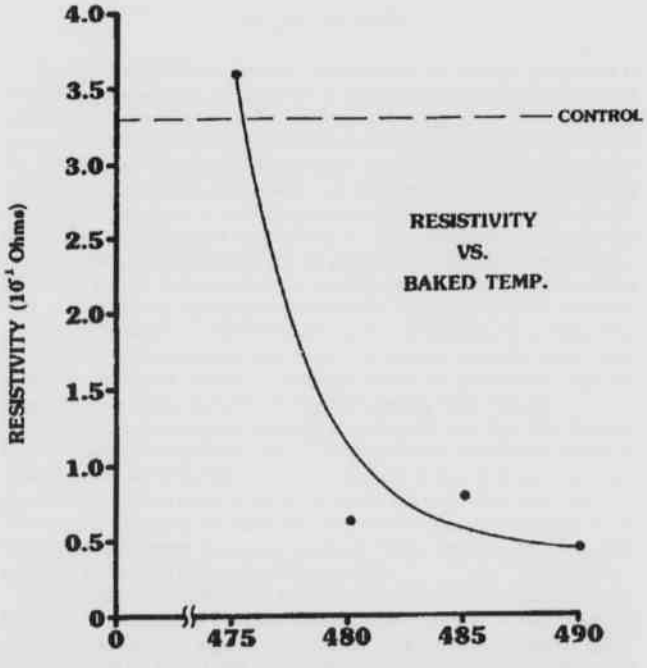

Figure 7. Resistivity versus firing temperature for the three coated surfaces.

Capacitance data are presented in Table 1. The data are suspect since the fixture used to sandwich the polyethylene film between the two coated squares was not designed to insure that the two plates were held together by the same force to cause the same interplate distance. However, the results (even though preliminary) do indicate that at approximately 480°C, the quasi-capacitor had a marked increase in measured capacitance. Further capacitance measurements are being readied using a constant pressure fixture and also variable polyethylene thicknesses (1 mil, 2 mil, and 3 mil). Substitution of manganese, iridium, and titanium in the coating mixtures are proposed in future studies.

Table 1

Firing Temperature (°C)	Capacitance (nF)
470	.1
475	.15
480	5
485	.2
490	.1

CONCLUSIONS

Resistivity of ruthenium oxide coatings were found to be extremely dependant upon the firing temperature and firing time. Ruthenium coatings show promise as the conductor plates in capacitors.

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